

Supplementary Information for:

**Cationic Polymers Bearing Quaternary Ammonium Groups-
Catalyzed CO₂ Fixation with Epoxides**

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Experimental Section

Materials

All chemicals were commercially available unless otherwise stated and used without further purification. Used chemicals were purchased either from Sigma Aldrich or Acros chemicals or Alfa Aesar. TLC was performed by using Fluka silica gel (0.2 mm) on aluminium plates. Silica-gel columns for chromatography were prepared with silica gel 60 (0.060–0.20 mesh ASTM) from Acros.

Instrumentation

Proton (^1H NMR) and carbon (^{13}C NMR) spectra were recorded on a Bruker Ascend 700 spectrometer equipped with a cryogenically cooled probe (TXI), or on a Bruker Avance 500 MHz spectrometer. ^{19}F NMR spectra were recorded on a Bruker Avance 300 MHz at 282.4 MHz. The chemical shifts are given in parts per million (ppm) on the delta scale (δ) and are referenced to the residual non-deuterated solvent for ^1H and TFA for ^{19}F . MALDI-TOF measurements were collected with a Bruker Autoflex III Smartbeam spectrometer and on an Agilent atmospheric pressure photoionization (APPI) source on an Agilent 6520 quadrupole time-of-flight (QTOF) in the positive mode.

Synthesis Procedures for the Ionene Polymers

Ionene polymers were synthesized via a two steps process as previously reported.^[1] Briefly, first step involves the amidation of *o*-, *m*- and *p*-phenylenediamine with 4-(chloromethyl)benzoyl chloride in the presence of Et₃N in CH₂Cl₂ to afford the corresponding bis-benzamides in good yields (75–98%) upon recrystallization. Subsequent copolymerization of the obtained bis-benzamides with the desired α,ω -diamine linker under equimolar conditions in DMF at 80 °C afforded white precipitates within 2–6 days. The resulting precipitates were filtered, washed (subsequently with DMF, CH₃CN and CH₂Cl₂) and dried under vacuum to give the desired pure polymers in modest yields (43–80%). Although we did not attempt to isolate the products from the supernatant liquid, TLC analysis of the reaction crude showed full conversion of the starting materials. Thus, the modest yields obtained during the synthesis of these ionenes could be due to some loss of material during the washing-filtration steps as well as to possible formation of small oligomers with insufficient size to precipitate from the reaction medium. In order to achieve adequate solubility and mobility of the polymers for GPC analysis, it was necessary to carry out counteranion exchange of chloride by TFSA or TFSI anions using LiTFSA or LiTFSI respectively in hot water. As expected for many step-growth polymers, these ionenes·TFSA are generally characterized by low degree of polymerizations ($n = 7\text{--}14$) and high dispersity values ($D = 2.1\text{--}5.7$).

The counteranion exchange from chloride to iodide was simply carried out by stirring the ionen in the presence of 10 equiv NaI in acetone for one night. Then the resulting residue was washed with acetone and H₂O. Ion chromatography revealed more than 80% exchange of the anion.

Table S1. Characterization parameters of ionenes.^a

Polymer	M_w (Da)	M_n (Da)	n	\mathcal{D}	ref.
A ^{1,2} ·TFSA	8.1×10^3	3.9×10^3	7	2.1	1
A ^{1,3} ·TFSA	1.2×10^4	5.0×10^3	7	2.4	1
A ^{1,4} ·TFSA	1.7×10^4	5.9×10^3	10	2.9	1
B ^{1,2} ·TFSA	1.6×10^4	6.1×10^3	9	2.6	2
B ^{1,3} ·TFSA	1.4×10^4	6.4×10^3	9	2.2	2
B ^{1,4} ·TFSA	1.4×10^4	6.4×10^3	12	2.1	2
C ^{1,2} ·TFSA	3.3×10^4	6.2×10^3	8	5.2	2
C ^{1,3} ·TFSA	3.8×10^4	6.6×10^3	9	5.7	2
C ^{1,4} ·TFSA	3.2×10^4	6.3×10^3	13	5.1	2
F·TFSI	2.8×10^3	1.7×10^3	13	1.6	3
E·TFSA	6.8×10^4	1.4×10^4	64	4.9	4

^a M_w = weight-average molecular weight; M_n = number-average molecular weight; n = number-average degree of polymerization; $\mathcal{D} = M_w/M_n$ = dispersity. ^b Counteranion exchange of other ionenes D was ineffective, at least in our hands.

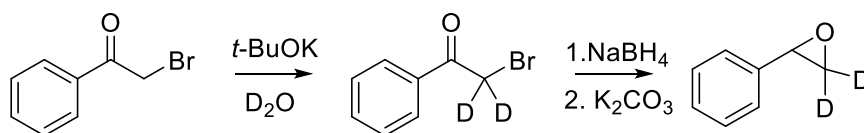
General experimental procedure for the CO₂ fixation with epoxides using ionene polymers

The reactions were carried out using a Radleys Carousel 12 Plus Reaction Station™. A mixture of 0.2 mmol of the corresponding ionene (based on the repeating monomeric catalytically active units of the ionene) was weighed in a reaction tube (ø 16mm). After the addition of 4 mmol epoxide and heating the mixture to 120 °C a CO₂ atmosphere was provided by using a simple balloon and stirring was started (1000 rpm). After the given reaction time the mixture was cooled down to room temperature and either filtered using a fritted glass funnel (P 4) to recover the ionenes or directly flushed through a short column of silica gel (heptanes/EtOAc = 10:1–3:1 as eluent) to afford the cyclic carbonates (**2**).

Recycling experiments:

The recycling experiments were carried out using phenyl glycidyl ether. After each reaction the reaction mixtures were filtered using a fritted glass funnel (P 4). The residue (ionene) was washed with 3 ml dichloromethane, dried under high vacuum and used again for the next experiment. The reactions showed more or less constant conversions (95% in first round, 95% in second round, 94% in third, 92% in the fourth round).

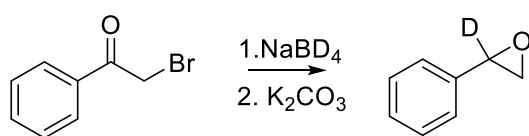
Preparation of terminal deuterated styrene oxide (**2a-D2**):



A solution of 2-bromo acetophenone (1999 mg, 10 mmol) in 5 mL CDCl₃ was cooled to 0 °C. Carefully *t*-BuOK (842 mg, 7.5 mmol) was added in small portions while the reaction mixture was heavily stirred. After 1 hour of stirring at 0 °C slowly 3 mL D₂O were added. A ¹H NMR sample of the CDCl₃ phase was recorded which showed a degree of deuteration of only 33 %. Additional *t*-BuOK (562 mg, 5.0 mmol) was then carefully added to the strongly stirred biphasic mixture, which was then stirred for 2 hours while allowing it to warm to room temperature. The phases were then separated and the aqueous phase was extracted with CDCl₃ (2x 2 mL). The combined organic phases were dried with Na₂SO₄ and the solvent was removed by rotatory evaporation. The crude product was then purified by column chromatography (silica gel, heptanes:EtOAc, 50:1→30:1) and 1.42 g (62 %) were afforded as white orange solid containing 90 % of fully deuterated product at the acidic α-position. Analytical data are in accordance with those reported in literature.^[8] ¹H NMR (300 MHz, δ, CDCl₃, 298 K): 4.42-4.47 (m, 0.21 H), 7.45-7.54 (m, 2H), 7.56-7.65 (m, 1H), 7.95-8.02 (m, 2H) ppm; ¹³C NMR (75 MHz, δ, CDCl₃, 298 K): 30.3 (qi, *J* = 22.5 Hz), 128.7, 128.8, 133.8, 133.9, 191.3 ppm

2-Bromo-1-phenylethan-1-one-2,2-d₂ (1400 mg, 7 mmol) was put into a Schlenk flask which was then evacuated and flushed with argon (3x) before adding 15 mL MeOH. This suspension was then cooled to 0 °C using an ice/salt/water bath. Portion wise NaBH₄ (294 mg, 7.7 mmol) was added and the reaction mixture was stirred for 3 hours while letting it warm up to room temperature. Then K₂CO₃ (968 mg, 7 mmol) was added at once and stirring was continued for 15 hours. The MeOH was removed by rotatory evaporation, 50 mL water were added and the aqueous phase was extracted with DCM (50 ml, 3x). The combined organic phases were washed with brine (50 mL), dried with Na₂SO₄ and the solvent was removed by rotatory evaporation. This afforded pure product (720 mg, 84 %) as a colorless liquid. Analytical data are in accordance with those reported in literature.^[9] ¹H NMR (300 MHz, δ, CDCl₃, 298 K): 2.78-2.83 (m, 0.15H), 3.12-3.18 (m, 0.15H), 3.86 (s, 1H), 7.25-7.40 (m, 5H) ppm; ¹³C NMR (75 MHz, δ, CDCl₃, 298 K): 51.5 (qi, *J* = 26 Hz), 52.1, 125.4, 128.1, 128.4, 137.5 ppm

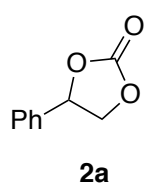
Preparation of styrene oxide deuterated in the benzylic position (2a-D1):



2-Bromo acetophenone (1000 mg, 5 mmol) was put into a Schlenk flask which was then evacuated and flushed with argon (3x) before adding 12 mL MeOH. This suspension was then cooled to 0 °C using an ice/salt/water bath. Portion wise NaBD₄ (210 mg, 5.5 mmol) was added and the reaction mixture was stirred for 3 hours, while letting it warm up to room temperature. Then K₂CO₃ (691 mg, 5 mmol) was added at once and stirring was continued for 20 hours. The reaction mixture was then filtered through a plug of Na₂SO₄ and the solvent was removed by rotatory evaporation. The crude product was then purified by column chromatography (silica gel, heptanes:EtOAc, 100:1→50:1) and 545 mg (91 %) were afforded as colourless liquid. Analytical data are in accordance with those reported in literature.^[10] ¹H NMR (300 MHz, δ, CDCl₃, 298 K): 2.84 (d, *J* = 5.5 Hz, 1H), 3.17 (d, *J* = 5.5 Hz, 1H), 7.26-7.41 (m, 5H) ppm; ¹³C NMR (75 MHz, δ, CDCl₃, 298 K): 51.0, 51.9 (t, 27 Hz), 125.4, 128.1, 128.4, 137.4 ppm

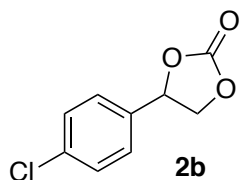
Analytical data of carbonates 2:

4-Phenyl-1,3-dioxolan-2-one (**2a**): Isolated yield: 614 mg (94%). Analytical data are in accordance with



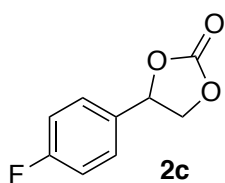
those reported in literature.^[5] ¹H NMR (300 MHz, δ , CDCl₃, 298 K): 7.48-7.39 (m, 3H), 7.38-7.33 (m, 2H), 5.67 (t, J = 8 Hz, 1H), 4.79 (t, J = 8.4 Hz, 1H), 4.43 (dd, J_1 = 8.6 Hz, J_2 = 7.9 Hz, 1H) ppm; ¹³C NMR (75 MHz, δ , CDCl₃, 298 K): 154.7, 135.7, 129.5, 129.0, 125.7, 77.8, 71.0 ppm; HRMS (ESI): m/z calcd for: C₉H₈NaO₃ [M+Na]⁺ 187.0371; found: 187.0367.

4-(4-Chlorophenyl)-1,3-dioxolan-2-one (**2b**): Isolated yield: 752 mg (95%). Analytical data are in



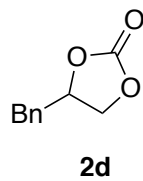
accordance with those reported in literature.^[5] ¹H NMR (300 MHz, δ , CDCl₃, 298 K): 7.42-7.34 (d, 2H, 8.5 Hz), 7.33-7.26 (d, 2H, 8.5 Hz), 5.65 (t, J = 8 Hz, 1H), 4.79 (t, J = 8.5 Hz, 1H), 4.28 (dd, J_1 = 8.6 Hz, J_2 = 7.8 Hz, 1H) ppm; ¹³C NMR (75 MHz, δ , CDCl₃, 298 K): 154.5, 135.4, 134.2, 129.2, 127.2, 77.1, 71.8 ppm; HRMS (ESI): m/z calcd for: C₉H₇ClNaO₃ [M+Na]⁺: 220.9981; found: 220.9978.

4-(4-Fluorophenyl)-1,3-dioxolan-2-one (**2c**): Isolated yield: 698 mg (96%). Analytical data are in



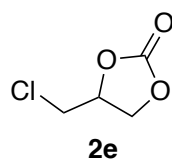
accordance with those reported in literature.^[5] ¹H NMR (300 MHz, δ , CDCl₃, 298 K): 7.41-7.30 (m, 2H), 7.17-7.06 (m, 2H), 5.66 (t, J = 8 Hz, 1H), 4.79 (t, J = 8.5 Hz, 1H), 4.31 (dd, J_1 = 8.6 Hz, J_2 = 7.8 Hz, 1H) ppm; ¹³C NMR (75 MHz, δ , CDCl₃, 298 K): 163.2 (d, J = 249 Hz), 154.6, 131.5 (d, J = 3.3 Hz), 127.9 (d, J = 8.5 Hz), 116.2 (d, J = 22.1 Hz), 77.4, 71.0 ppm; ¹⁹F NMR (282 MHz, δ , CDCl₃, 298 K): -111.1 ppm HRMS (ESI): m/z calcd for: C₉H₇FNaO₃ [M+Na]⁺: 205.0277; found: 205.0271.

4-Benzyl-1,3-dioxolan-2-one (**2d**): Isolated yield: 794 mg (95%). Analytical data are in accordance with



those reported in literature.^[6] ¹H NMR (300 MHz, δ , CDCl₃, 298 K): 7.40-7.28 (m, 3H), 7.26-7.21 (m, 2H), 5.01-4.91 (m, 1H), 4.46 (t, J = 8.2 Hz, 1H), 4.18 (dd, J_1 = 8.6 Hz, J_2 = 6.9 Hz, 1H), 3.16 (dd, J_1 = 14.2 Hz, J_2 = 6.3 Hz, 1H), 3.01 (dd, J_1 = 14.1 Hz, J_2 = 6.1 Hz, 1H) ppm; ¹³C NMR (75 MHz, δ , CDCl₃, 298 K): 154.7, 133.8, 129.2, 128.8, 127.4, 76.7, 68.4, 39.4 ppm; MS (ESI): m/z calcd for: C₁₀H₁₄NO₃ [M+NH₄]⁺: 196.1; found: 196.1.

4-(Chloromethyl)-1,3-dioxolan-2-one (**2e**): Isolated yield: 519 mg (95%). Analytical data are in

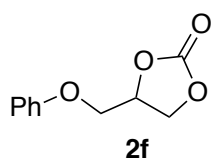


2e

accordance with those reported in literature.^[5] ¹H NMR (300 MHz, δ , CDCl₃, 298 K): 5.04-4.91 (m, 1H), 4.59 (t, J = 8.2 Hz, 1H), 4.41 (dd, J_1 = 5.5 Hz, J_2 = 8.0 Hz, 1H), 3.83-3.68 (m, 2H) ppm; ¹³C NMR (75 MHz, δ , CDCl₃, 298 K): 154.3, 74.3, 66.7, 44.1 ppm;

HRMS (ESI): m/z calcd for: C₄H₅ClNaO₃ [M+Na]⁺: 158.9825; found: 158.9821.

4-(Phenoxymethyl)-1,3-dioxolan-2-one (**2f**): Isolated yield: 743 mg (94%). Analytical data are in

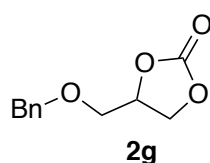


2f

accordance with those reported in literature.^[5] ¹H NMR (300 MHz, δ , CDCl₃, 298 K): 7.31 (t, J = 7.8 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 8.1 Hz), 5.09-4.96 (m, 1H), 4.60 (t, J = 8.5 Hz, 1H), 4.51 (dd, J_1 = 6.0 Hz, J_2 = 8.4 Hz, 1H), 4.24 (dd, J_1

= 10.5 Hz, J_2 = 3.8 Hz, 1H),), 4.12 (dd, J_1 = 10.5 Hz, J_2 = 3.8 Hz, 1H) ppm; ¹³C NMR (75 MHz, δ , CDCl₃, 298 K): 157.7, 154.7, 129.5, 121.8, 114.5, 74.1, 66.7, 66.1 ppm; HRMS (ESI): m/z calcd for: C₁₀H₁₀NaO₄ [M+Na]⁺: 217.0477; found: 217.0475.

4-((Benzyloxy)methyl)-1,3-dioxolan-2-one (**2g**): Isolated yield: 794 mg (95%). Analytical data are in

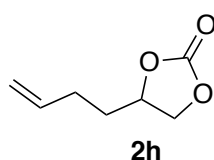


2g

accordance with those reported in literature.^[7] ¹H NMR (300 MHz, δ , CDCl₃, 298 K): 7.27-7.40 (m, 5H),), 4.75-4.85 (m, 1H), 4.58 (dd, J_1 = 17.5 Hz, J_2 = 12.0 Hz, 2H), 4.45 (t, J = 8.4 Hz, 1H), 4.35 (dd, J_1 = 8.4 Hz, J_2 = 6.0 Hz, 1H), 3.70 (dd, J_1 = 11.0 Hz, J_2 = 3.7 Hz, 1H) 3.59 (dd, J_1 = 11.1 Hz, J_2 = 3.7 Hz, 1H) ppm;

¹³C NMR (75 MHz, δ , CDCl₃, 298 K): 154.9, 137.0, 128.3, 127.8, 127.5, 74.9, 73.4, 68.7, 66.1, ppm; MS (ESI): m/z calcd for: C₁₁H₁₂NaO₄ [M+Na]⁺: 231.1; found: 231.1.

4-(But-3-en-1-yl)-1,3-dioxolan-2-one (**2h**): Isolated yield: 275 mg (48%). Analytical data are in

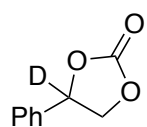


2h

accordance with those reported in literature.^[5] ¹H NMR (300 MHz, δ , CDCl₃, 298 K): 5.84-5.66 (m, 1H), 5.10-4.96 (m, 2H), 4.77-4.63 (m, 1H), 4.50 (t, J = 8.1 Hz, 1H), 4.05 (t, J = 7.8 Hz, 1H), 2.32-2.05 (m, 2H), 1.98-1.81 (m, 1H), 1.81-1.65 (m, 1H) ppm; ¹³C NMR (75 MHz, δ , CDCl₃, 298 K): 154.9, 136.0, 116.1, 76.2, 69.2, 32.8, 28.4

ppm; HRMS (ESI): m/z calcd for: C₇H₁₀NaO₃ [M+Na]⁺: 165.0528; found: 165.0526.

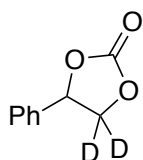
(S11) 4-Phenyl-1,3-dioxolan-2-one-4-d (**2a-D1**): ^1H NMR (300 MHz, δ , CDCl_3 , 298 K): 7.46-7.25 (m, 5H),



2a-D1

4.79 (d, $J = 8.6$ Hz, 1H), 4.33 (d, $J = 8.6$ Hz, 1H) ppm; ^{13}C NMR (75 MHz, δ , CDCl_3 , 298 K): 154.7, 135.6, 129.6, 129.1, 125.8, 77.8 (t), 71.0 ppm; MS (ESI): $\text{C}_9\text{H}_7\text{DNaO}_3$ [$\text{M}+\text{Na}$] $^+$ 188.0; found: 188.0.

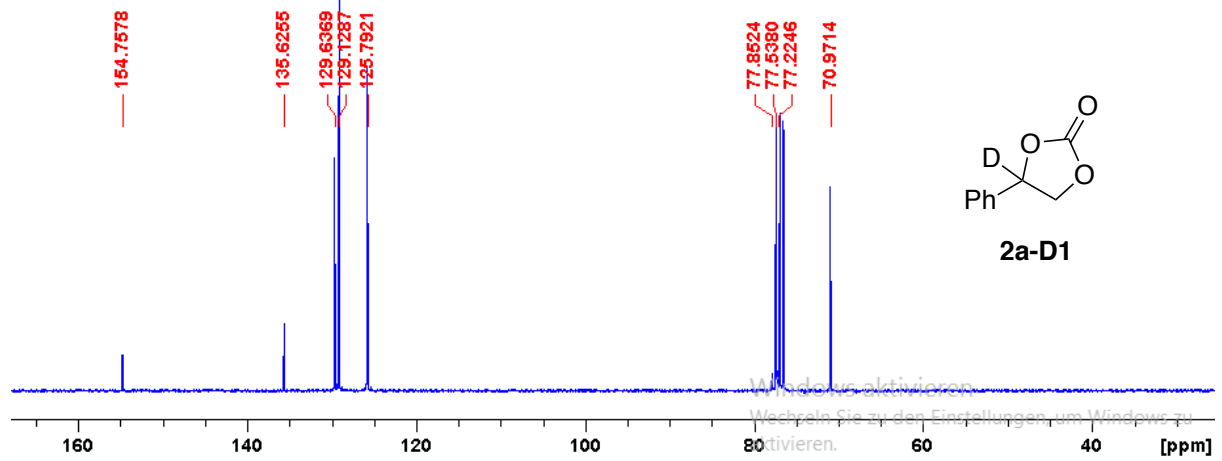
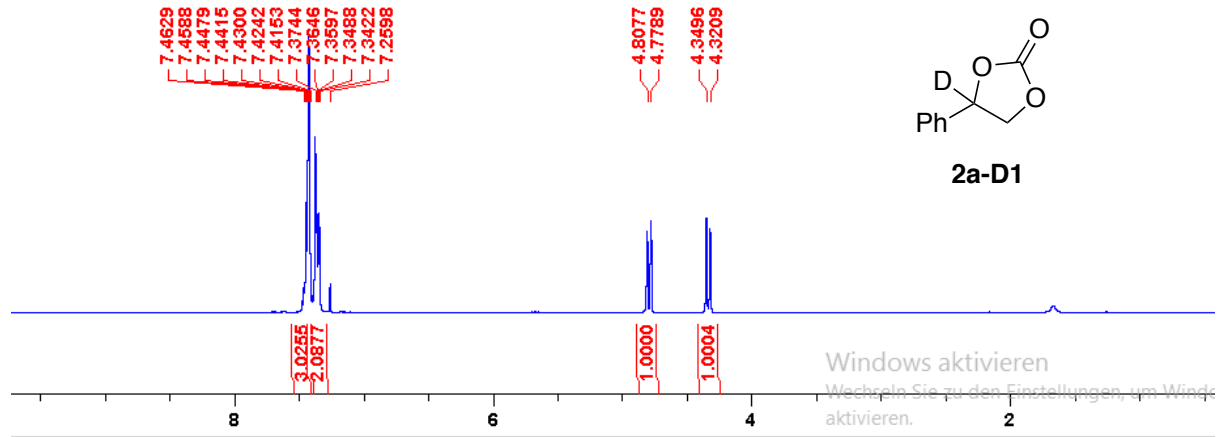
4-Phenyl-1,3-dioxolan-2-one-5,5-d2 (**2a-D2**): ^1H NMR (300 MHz, δ , CDCl_3 , 298 K): 4.35 (m, 0.14H), 4.80

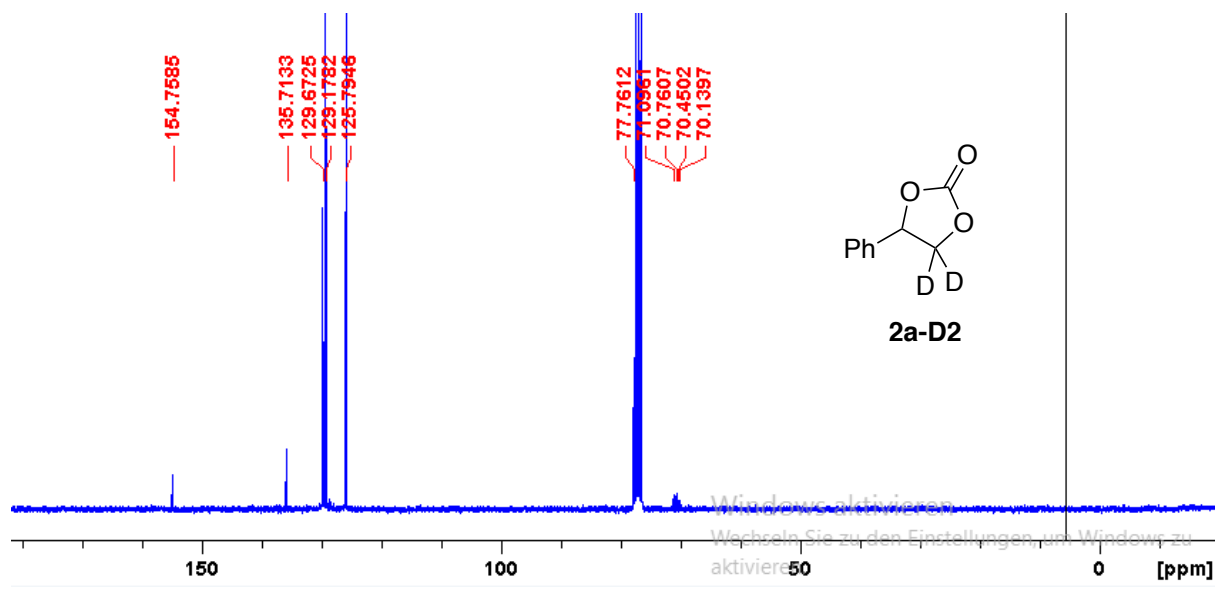
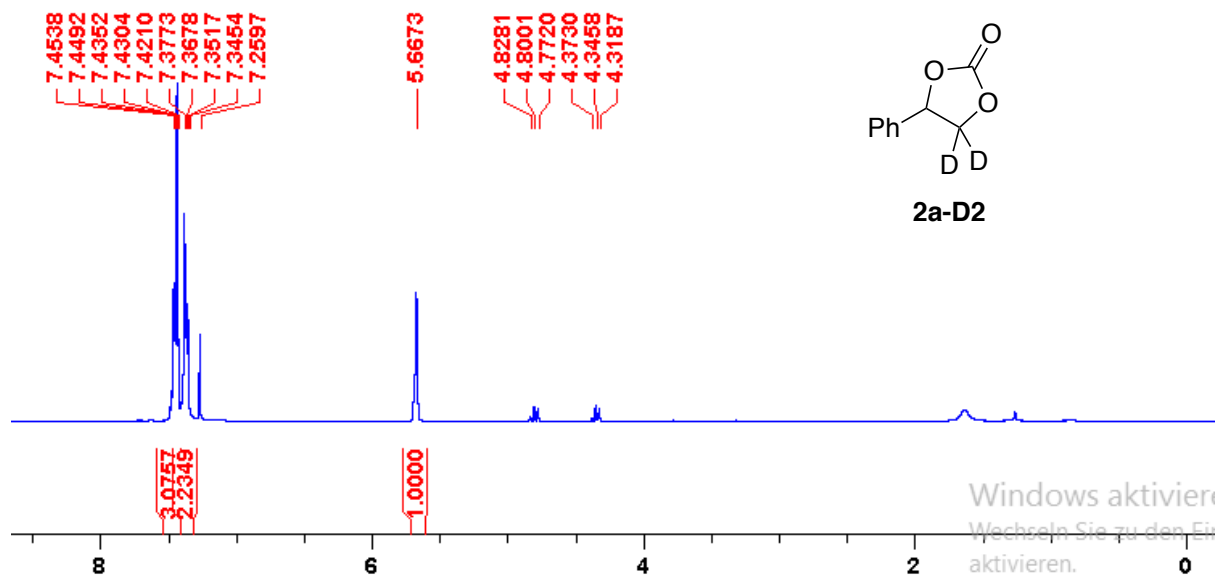


2a-D2

(m, 0.14H), 5.66 (s, 1H), 7.33-7.38 (m, 2H), 7.40-7.48 (m, 3H) ppm; ^{13}C NMR (75 MHz, δ , CDCl_3 , 298 K): 71.0 (q, $J = 24$ Hz), 77.8, 125.8, 129.2, 129.7, 135.7, 154.8 ppm; MS (ESI): $\text{C}_9\text{H}_6\text{D}_2\text{NaO}_3$ [$\text{M}+\text{Na}$] $^+$ 189.1; found: 189.1.

NMR copies of deuterated carbonates 2a:





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